Resource utilization of organic spent adsorbent to prepare three-dimensional sulfate-functionalized layered double oxide for superior removal of azo dye

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1 **Resource utilization of organic spent adsorbent to**
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Abstract

Developing superior, rapid, cost-effective adsorbents derived from organic spent adsorbent is an economically sustainable way for purifying azo dye wastewater. Herein, we report a precursor-calcination strategy for the recycle of the organic spent adsorbent to a high value-added three-dimensional sulfate-functionalized MgAl-layered double oxide (3S-LDO). Thanks to the unique property of the sulfate group and LDO, 3S-LDO exhibited a superior (4340.71 mg/g) and ultrafast (<1 hour) adsorption toward methyl orange (MO, as the representative of azo dye). A thermodynamic study revealed that the reaction process was spontaneous and exothermic. FT-IR, XPS, and XRD results confirmed that the sulfate from 3S-LDO played a vital role in MO removal wherein the S=O bond (with the electrophilic character) from SO_4^{2-} interacted with the N=N double bond (with rich electron) in MO through the electron donor-acceptor mechanism. And the “memory effect” and surface complexation of 3S-LDO further strengthened the MO adsorption. More importantly, 3S-LDO could work efficiently in a wide pH range and even in the presence of competitive anions (*e.g.*, Cl^- , NO_3^- , and CO_3^{2-}). Multiple cyclic runs and selective tests demonstrated the excellent reusability and explicit selectivity of 3S-LDO. This work not only provides a prospective sulfate-functionalized adsorbent from organic waste for rapid azo dye removal from wastewater but also achieves the high value-added utilization of organic waste.

Keywords

Organic spent adsorbent · Sulfate-functionalized layered double oxide · Methyl orange · Superior adsorption · Regeneration · Removal mechanism

Introduction

Excessive discharge of organic dyes has already caused severe risk to the ecological system and human health (Ji et al. 2021). Particularly, azo dyes are proven to be more toxic, carcinogenic, and even mutagenic compared to other forms of dyes, which are composed of aromatic rings and covalent azo bonds ($N=N$) (Gurav et al. 2021; Kelm et al. 2019; Oon et al. 2020). Over the past few decades, a vast of strategies, such as catalytic (Fu et al. 2019), photocatalytic degradations (Riaz et al. 2020), adsorption (Khaled et al. 2020), membrane (Yang et al. 2020), filtration (Mohtor et al. 2017), have been conducted on the elimination of azo dye from wastewater. However, challenges inherent to azo dye removal still include expensive cost, low-efficiency, poor regeneration, or membrane fouling, hindering their large-scale applications. Therefore, it is still an urgent requirement to develop a technique with preeminent ability, rapid kinetic, cost-efficiency, and outstanding reusability for azo dye wastewater treatment.

Layered double hydroxides (LDHs), known as a class of 2:1 type anionic clay minerals, are gaining widespread attention in water purification due to their flexible layered crystal structure, ion-exchange ability, and “memory effect” (Chen et al. 2021; Hu et al. 2020; Li et al. 2020). It is worth mentioning that the “memory effect” is primarily responsible for endowing LDHs applied in organic wastewater treatment. That is, after LDHs effectively capturing organics from the water via ion-exchange and/or surface adsorption, the spent LDHs can be calcined at moderate temperatures to form the layered double oxides (LDOs), which can restructure to LDHs via rehydrate based on the “memory effect”. (Kundu and Naskar 2019; Lv et al. 2018; Vu and Wu 2020). In fact, LDOs have been reported as environmental remediation

agents for pollutants elimination from the water with superior capacity and reusability. Zhang *et al.* reported that the rhombic dodecahedral CaAl-LDO obtained by the calcination of spent CaAl-LDH exhibited a high adsorption capacity (~500 mg/g) for Congo red and high removal efficiency (93%) after five consecutive cycles (Zhang *et al.* 2018). Our previous works also found that the hierarchical organic MgAl-LDH (O3D-LDH) possessed excellent reusability after MO adsorption based on the formation of MgAl-LDO in four continuous cycles (Zhang *et al.* 2019b). LDOs can be served as the high value-added products of organic spent LDHs to resolve the recovery of the LDHs applied in the organic wastewater treatment. In recent, with the deeper concept of resource utilization, researchers have constantly focused on the adsorbed organic compounds with valuable elements such as C, S and N, which can be converted into useful functional components (Laipan *et al.* 2015; Rong *et al.* 2020; Tang *et al.* 2017; Wan *et al.* 2019). Take sulfur as an example, the sulfate group resulted from S recovery can enhance such adsorbents for azo dye, since the electron-withdrawing property of sulfate exhibits a strong affinity toward electron-rich N=N bond of azo dye (Feng *et al.* 2020; Han *et al.* 2016; Zhao *et al.* 2011). Inspired by these researches, if the spent LDHs adsorbed sulfur-containing organics are exploited to synthesize a sulfate-dropped functional renewable LDO, it will not only offer a promising capture agent for azo dye but also achieve the resource utilization of organic spent waste.

In our previous works, we had successfully captured sodium dodecyl sulfate (SDS, persistent organic pollutants) with LDH to generate 3D S-containing MgAl-LDH (3S-LDH) (Zhang *et al.* 2019a). Herein, we attempted to employ 3S-LDH as the precursor to fabricate 3D sulfate-functionalized MgAl-LDO (denoted as 3S-LDO) through calcination examined by X-

ray diffraction (XRD), the Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and transmission electron microscopy (TEM). To investigate the adsorption performance of 3S-LDO toward azo dyes, methyl orange (MO), with two aromatic rings and azo fragment, was selected as a representative target contaminant (Siyasukh et al. 2018). The effect of various experimental conditions (adsorbent dosage, contact time, initial concentration, temperature, and ion strength) was systematically investigated. And the interaction mechanism between MO and 3S-LDO was further revealed via microstructure analysis. Additionally, the reusability, selective performance, and the adsorption ability of 3S-LDO in real waters were investigated as well.

Material and methods

Materials

Magnesium nitrate hexahydrates ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), urea (H_2NCONH_2), sodium dodecyl sulfate (SDS, $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$), citric acid (CA, $\text{C}_6\text{H}_8\text{O}_7$) and methyl orange (MO) with analytical grade were purchased from Aladdin Chemicals Reagent Company (Shanghai, China). Ltd and used without further purification. Solutions used in the experiments were carried out with deionized water.

The tap water, river water, and industrial wastewater were collected from the laboratory, Jiangxi before the lake, and a factory in Jiujiang, Jiangxi province, respectively. The freshwater samples were previously filtered with qualitative filter paper (Jiao Jie, China) upon arrival and stored at 4 °C in a refrigerator.

Preparation of samples

In general, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1500 g), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.2051 g), and urea (0.2402 g) were dissolved in 50 mL deionized water. Subsequently, SDS solution (30 mL) with the initial concentrations of 0.1 M was immediately added into above mixed solution. After vigorously stirring (30 min) and ultrasonication (30 min), the suspension was transferred into a Teflon lining stainless steel autoclave and treated at 150 °C for 6 h. Finally, the precipitation, *i.e.*, 3S-LDH, was collected via centrifugation and dried at 70 °C for 6 h. To prepare 3S-LDO, 3S-LDH was heated at 700 °C in a muffle furnace for 4 h.

For comparison, sulfate-free 3D-LDH was prepared in the same way with 3S-LDH except using citric acid instead of SDS (Cao et al. 2019). Then, 3D-LDO was obtained via the calcination of 3D-LDH at 700 °C. The successful synthesis of 3D-LDH and 3D-LDO was confirmed by XRD and FT-IR, and SEM (Fig. S1).

Adsorption experiments

Batch experiments were conducted as follows. The effect of adsorption dosage was investigated with different 3S-LDO dosages (0.1, 0.3, 0.5, 0.7, 1.0 g/L). The adsorption isothermal experiments for MO removal by 3S-LDO and 3D-LDO were carried out with the initial MO concentrations of 20-4000 mg/L at diverse temperatures (25, 35, and 45 °C), respectively. For adsorption kinetic, the experiments were performed at various intervals (0-12 h) with different MO concentrations (10, 1000, and 2000 mg/L for 3S-LDO; 1000 mg/L for 3D-LDO). The pH effect was investigated in the range of 3-11, which was adjusted by 0.1 M HCl/NaOH. Moreover, the influence of ionic strength on MO removal was studied by adding

Cl⁻, NO₃⁻, and CO₃²⁻ at various concentrations (0.02, 0.04, 0.06, 0.08, and 0.1 M). For all tests, a certain quantity of 3S-LDO or 3D-LDO was added to the 10 mL MO solution. The mixture was shaken at 150 rpm for 12 h and filtered through a 0.45 µm polycarbonate membrane. The residual MO concentrations were analyzed using a UV-vis spectrophotometer (V-1600 spectrophotometer) at a wavelength of 463 nm (Siyasukh et al. 2018).

The adsorption capability and efficiency were calculated according to the formulas:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

Where q_e (mg/g) is the adsorption amount of MO per gram of absorbents at equilibrium time. C_0 and C_e (mg/L) represent MO concentrations in supernatants at initial and equilibrium conditions, respectively. V (L) is the solution volume, m (g) refers to the mass of the adsorbent.

A selective adsorption experiment of dyes was performed by adding 3 mg of 3S-LDO in 10 mL of dye mixture solution containing 100 mg/L MO and 50 mg/L MB. The equilibrium concentration of the mixture solution was calculated by UV-vis spectra.

Solid preparation

0.03 g 3S-LDO was added to 100 mL MO solution with concentrations of 20, 1000, and 2000 mg/L, respectively. The mixture was stirred at 150 rpm for 12 h. After centrifuging, the precipitates were collected and dried at 60 °C. The samples were denoted as 3S-LDO_MO₂₀, 3S-LDO_MO₁₀₀₀, and 3S-LDO_MO₂₀₀₀, respectively.

Characterization

The morphology of as-prepared material was determined on transmission electron microscopy (TEM, JEOL-2010) with high-resolution TEM (HRTEM, JEOL-2010) image at an accelerating voltage of 200 kV, and scanning electron microscope (SEM, JSM 6701F) equipped with energy-dispersive X-ray spectroscopy (EDS) mapping. The chemical composition and crystallographic structure were carried out by using an X-ray powder diffractometer (XRD, D8 ADVANCE X) equipped with Cu K α (40 kV, 40 mA) radiation. The elemental chemical states were characterized by Fourier transformed infrared spectroscopy (FT-IR, TNA 370) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI). The specific surface area and pore diameter of the samples were analyzed by the Brunauer-Emmett-Tellersurface method measured using an ASAP 2460 surface analyzer.

Recycle experiments

The reusability and stability of 3S-LDO were evaluated by adsorption-regeneration experiments. The protocol of MO adsorption was the same as that in section 2.3. The regeneration was carried out by calcinating the used adsorbent after reaction in a muffle furnace at 700 °C for 4 h in air. Then the collected material was reused for MO adsorption in the succeeding cycles.

Result and discussion

Characterization of 3S-LDO

The phase compositions of 3S-LDH precursor and 3S-LDO were detected by the XRD technique. As displayed in Fig. 1a, a set of characteristic peaks of MgAl LDH with the d -spacing value ($d_{(003)}$) of 2.72 nm as well as the broad peak assigned to SDS located at 20.5° (JCPDS NO. 39-1996) can be observed for the 3S-LDH sample. This affirmed that the as-prepared precursor was the organic MgAl LDH loaded with SDS, in good agreement with previous literatures (Li et al. 2008; Zhang et al. 2019b). After calcination, a clear transformation of the crystalline phase from LDH to LDO (MgAl_2O_4 , marked with green) was detected in the 3S-LDO (Fig. 1a) (Lei et al. 2017). Moreover, several new MgSO_4 peaks with (021), (111), (022), (131), (042), and (231) crystalline planes (JCPDS NO. 21-0546) were identified in the 3S-LDO, while the relative organic phases of SDS disappeared. Such phenomenon suggested that the SDS was completely converted to sulfate group loaded on LDO during calcination.

FT-IR was employed to investigate the chemical structure of 3S-LDO and 3S-LDH (Fig. 1b). For the 3S-LDH, the wide bands centered at 3530 , 1639 and 445 cm^{-1} were ascribed to the hydroxyl group, the interlayer water molecules, and the O-M-O band, respectively (Ji et al. 2018). And two apparent characteristic S=O bands of SDS emerged at 1463 and 1210 cm^{-1} (Zhang et al. 2019b). After calcination, the characteristic peak of hydroxyl groups and interlayer water all diminished. Meanwhile, O-M-O band of 3S-LDH was divided into several new peaks corresponding to M-O (M: Mg or Al) at the low wavenumber region ($400\text{-}800\text{ cm}^{-1}$). The results affirmed that the precursor LDH was dehydrated to form LDO during the calcination process

(Nath and Dolui 2018). Notably, the SDS peaks vanished in 1463 and 1210 cm^{-1} accompanying by the occurrence of a sharp peak at 1114 cm^{-1} ascribed to the SO_4^{2-} in the 3S-LDO (Yu et al. 2020). The SDS in 3S-LDH was successfully transformed to SO_4^{2-} .

XPS measurement was further conducted to investigate the chemical composition and chemical state of elements and surfaces in the 3S-LDO. The survey XPS spectrum (Fig. 1c) demonstrated the presence of O, Al, Mg, and S elements in 3S-LDO. In the high-resolution Mg 1s XPS spectrum (Fig. 1d), two peaks emerged at approximately 1304.5 eV ascribed to Mg-O bond derived from MgAl_2O_4 and 1303.2 eV belonged to the Mg-S bond (Yuan et al. 2014). Notably, the S was attributed to the SO_4^{2-} group as demonstrated by the high-resolution S 2p and O 1s spectra (Fig. 1e and f) (Li et al. 2020; Zhang et al. 2016). Therefore, we could speculate that the SO_4^{2-} bonded to Mg^{2+} from MgAl_2O_4 via the formation of the Mg-S bond to be anchored in 3S-LDO. To further affirm the hypothesis, we added 0.01 g 3S-LDO into 10 mL deionized water to investigate the release of SO_4^{2-} after 12 h. As described in Table S1, it was found that only 4.41 mg/L of SO_4^{2-} was released into the solution. Theoretically, the amount of SO_4^{2-} in 3S-LDO should be calculated as 295.16 mg/L according to the atomic percentage of S from 3S-LDO (9.27%) in the survey XPS spectrum (Fig. 1c), which was significantly higher than that of the actual release value, indicating that SO_4^{2-} in 3S-LDO was almost insoluble in water. Therefore, it could be confirmed the strong interaction between SO_4^{2-} and 3S-LDO.

The morphology of the 3S-LDO was observed by SEM and TEM images (Fig. 2a and b). It exhibited a flower-like microstructure with an average diameter of $\sim 3 \mu\text{m}$, which resembled the typical 3D structure of LDO (Hong et al. 2020). HRTEM image (Fig. 2c) observed the lattice fringes with the interplanar spacings of 0.258 nm, which linked to the (311) plane of

LDO (MgAl_2O_4). Element mapping images in Fig. 2d presented that not only Mg, Al, and O of LDO but also S elements were homogeneously distributed on the 3S-LDO's surface, confirming the construction of sulfate-functionalized LDO.

Adsorption of MO on 3S-LDO

Effect of adsorbent dosage

Fig. 3a showed the effect of adsorbent dosage (0.1-1.0 g/L) on the MO removal. With the dosage raising, the adsorption capacity of 3S-LDO decreased, whereas the removal efficiency initially ascended dramatically due to the increase of the unsaturated adsorption sites (Maity and Ray 2017), until reaching a plateau at 0.3 g/L. Considering the removal efficiency and cost of wastewater treatment applications, the dosage of 3S-LDO was set as 0.3 g/L in the subsequent experiments. It is worth noting that the obtained adsorption amount and efficiency kept a high level (3452.37 mg/g and 95.41%) at this low 3S-LDO dosage (only 0.3 g/L) with the MO concentration of 1000 mg/L, indicating that 3S-LDO was an excellent adsorbent toward MO.

Effect of initial concentration and adsorption isotherm

Adsorption isotherms were employed to investigate the adsorption capacities of 3S-LDO at various initial MO concentrations (C_0) under 25, 35, and 45 °C, respectively. As is apparent from Fig. 3b, MO removal exhibited a nearly linear relationship with C_0 and reached adsorption equilibrium at 2000 mg/L. While for the removal rate (Fig. 3c), it showed an extreme uptrend at initial low concentration (≤ 400 mg/L), followed by a temporary plateau, and gradually

dropping when the MO concentration was higher than 1000 mg/L. Compared to the removal efficiency of 3D-LDO (Fig. 3d), it was different from 3D-LDO, implying the involvement of other interactions for MO removal besides LDO. Additionally, the adsorption capacities of 3S-LDO decreased with the elevated temperature. The result suggested that lower temperature favored the MO removal by 3S-LDO, which was the desirable attribute for water treatment as well (Zhao et al. 2014).

The Langmuir (Eq. (3)) and Freundlich (Eq. (4)) models were employed to further analyze the obtained adsorption data (Demirçivi 2018). Based on the discussion on the impact of initial concentration (Fig. 3c), the adsorption isotherms model was examined in the concentration range of 800-4000 mg/L for 3S-LDO.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where C_e (mg/L) and q_e (mg/g) are the equilibrium adsorption concentration and capacity, respectively; b (L/mg) is the Langmuir isothermal constant and q_m (mg/g) is the maximum adsorption capacity; K_F [(mg/g)·(L/mg)^{1/n}] and n are the Freundlich empirical constants and heterogeneity factor, respectively.

The fitting results were presented in Fig. S2 and Table 1. According to the value of the correlation coefficients (R^2), the Langmuir model gave a better fit than the Freundlich model, suggesting the occurrence of monolayer adsorption in the investigated concentration ranges (Zhang et al. 2019c). Notably, the theoretical maximum adsorption amounts of 3S-LDO calculated from the Langmuir model were much higher than that of 3D-LDO under the same conditions, indicative of the crucial role of the sulfate group in 3S-LDO on enhancing MO

adsorption. Besides, it should also be pointed out that the q_m (4340.71 mg/g) of 3S-LDO at 25 °C was much superior to those of the reported materials (Table 2), highlighting the exceptional performance of 3S-LDO for MO.

Thermodynamic analysis

The temperature effect on the MO adsorption by 3S-LDO was explored by thermodynamic analysis. Three basic thermodynamic parameters, including standard enthalpy change (ΔH^0), entropy change (ΔS^0) and Gibbs free energy change (ΔG^0), were employed and calculated as follows (Wu et al. 2018).

$$K_d = \frac{q_e}{C_e} \quad (5)$$

$$\Delta G^0 = -RT \ln K_d \quad (6)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

where K_d (L/g) is the equilibrium constant at various temperatures, R (8.314 J/(mol·K)) is the universal gas constant and T (K) is the system temperature; The values of ΔH^0 and ΔS^0 are obtained from the slope and the intercept of $\ln K_d$ (Fig. 3e). The thermodynamic parameters were listed in Table S2.

The ΔH^0 values of 3S-LDO was -13.79 kJ/mol, indicating that MO adsorption on the sample was exothermic (Wang et al. 2015). The negative ΔS^0 values demonstrated that the freedom feature of the adsorption systems became lower after adsorption, which ascribed to the restriction of molecular motion on the surface of adsorbents (Wang et al. 2015). From the negative values of ΔG^0 for 3S-LDO in all temperatures, it can be concluded that the reaction process was spontaneous and favorable. In addition, the ΔG^0 values increased with increasing

temperature confirming that the lower temperature favored the MO adsorption on 3S-LDO (Zhao et al. 2014), which was per the results of adsorption isotherm (Fig. 3b).

Effect of contact time and adsorption kinetics

Given the significant influence of initial MO concentration on 3S-LDO (Fig. 3c), the kinetic was conducted at three different initial MO concentrations (20, 1000, 2000 mg/L). As time increased (Fig. 3f), the adsorption amount had a trivial increase at low MO concentration (20 mg/L), while the adsorption was very fast when the MO concentration ≥ 1000 mg/L, with the adsorption capacity up to 2720.27 mg/g in the first 1 minute (Fig. 3f and inset). These distinct kinetic results at low and high MO concentration verified that the removal process relied on initial dye concentration. And the fast-kinetic at high MO concentration (≥ 1000 mg/L) placed 3S-LDO in a notable position among advanced materials for MO removal. By contrast, the adsorption rate of 3D-LDO was much slower than 3S-LDO (Fig. S3), inferring that the rapid adsorption performance of 3S-LDO was also relative with the sulfate group.

To further investigate the detailed adsorption dynamics, the pseudo-first-order model (Eq. (8)) and pseudo-second-order model (Eq. (9)) were used to simulate the experimental data. The two kinetic models were expressed as follows (Wang et al. 2015):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and time t (min), respectively; k_1 (min^{-1}) and k_2 [$\text{g}/(\text{mg} \cdot \text{min})$] are the kinetic adsorption rate constants of the pseudo-first-order and pseudo-second-order models, respectively.

The kinetics data were presented in Fig. S4, and the corresponding parameters were listed in Table 3. From the R^2 of these models, the pseudo-second-order model was more suitable to describe the MO removal, with the closer calculated $q_{e,cal}$ to the values of experiments ($q_{e,exp}$). This unveiled that chemisorption was the primary adsorption mechanism (Yao et al. 2017). Compared to 3D-LDO (1.43×10^{-3} g/(mg·min)) in Table 3, the k_2 for 3S-LDO (5.94×10^{-3} g/(mg·min)) was much higher, *i.e.*, the MO adsorption on 3S-LDO was faster than 3D-LDO, proving again that the important role of sulfate group in the enhancement of MO adsorption rate.

Adsorption mechanism

Generally, the specific surface area (SSA) of adsorbent has a positive influence on contaminants removal (Sun et al. 2020), that is, the higher SSA is beneficial for contaminants removal (Li et al. 2020). As depicted in Fig. S5, 3S-LDO exhibited a typical type-IV isotherm with a narrow hysteresis loop (H3 type) like that of 3D-LDO (Siyasukh et al. 2018). Interestingly, the value of SSA for 3S-LDO was markedly lower than that of 3D-LDO (Table S3), while the adsorption capacity of 3S-LDO (4340.71 mg/g) was superior to 3D-LDO (3594.46 mg/g) in Fig. 3b. It can be implied that the SSA was not the dominant reason leading to the excellent removal performance of 3S-LDO toward MO.

To clearly understand the removal mechanisms, the physicochemical structures of the 3S-LDO before and after MO removal were investigated at various dye concentrations (20, 1000, and 2000 mg/L). The FT-IR results (Fig. 4a) validated that 3S-LDO successfully captured MO in all concentrations, as evidenced by the appearance of MO characteristic peaks in the resulting

products, such as 1606 and 1518 cm^{-1} (the C=C stretching vibration of benzene ring structure),
 1370 and 1420 cm^{-1} (the N=N stretching vibration) (Han et al. 2016), 1187 and 1034 cm^{-1} (the
 asymmetric and symmetric stretching vibrations of SO_3^- group in MO), 1117 cm^{-1} (the C-N
 stretching vibration) (Yao et al. 2017). With the increasing MO concentration, the intensity of
 SO_3^- peak in MO enhanced while that of SO_4^{2-} bond in 3S-LDO became weak, indicating that
 the SO_4^{2-} of 3S-LDO reacted with MO (Fig. 4a). In addition, the M-O (M=Mg and Al) bonds
 at 400-900 cm^{-1} in the FT-IR spectra shifted or disappeared in all concentrations (Fig. 4b),
 implying that the complexation might exist in MO removal due to metal ions (*i.e.*, Mg^{2+} and
 Al^{3+}) from 3S-LDO complexed with SO_3^- groups of MO (Lyu et al. 2020; Yao et al. 2017; Zhang
 et al. 2018). And the obvious shift of Mg 1s and Al 2p XPS spectra before and after MO
 adsorption also proved the complexation (Fig. 4c) (Peng et al. 2014). The interaction between
 SO_4^{2-} and MO also was further examined by the XPS spectra of S 2p and N 1s (Fig. 4d and e).
 The obvious redshift of SO_4^{2-} peak and blueshift of N=N peak was observed with the increase
 of MO concentration (Wang et al. 2018). Generally, the S=O bond from SO_4^{2-} with a covalent
 double bond exhibited stronger affinity towards electrons (Zhao et al. 2011), while the N=N
 double bond in MO as an electron rich bond could provide the electrons (Han et al. 2016). It
 could be illustrated that the electron-donor-acceptor (EDA) interaction occurred between the
 N=N double bond in MO and the S=O bond from SO_4^{2-} of 3S-LDO (Sun et al. 2020; Yuan et
 al. 2020). Besides, the MO peaks, *i.e.*, SO_3^- in S 2p spectrum and $-\text{N}(\text{CH}_3)_2$ in N 1s spectrum,
 appeared in high concentrations of MO, which indicated that the EDA interaction was
 reinforced with the increase of MO concentration. (Jiang et al. 2020; Zhang et al. 2019b).
 Especially, the N-S bond was checked at 400.0/400.2 eV in N 1s spectrum, further confirming

the strong interaction between the SO_4^{2-} and MO (Setiawan et al. 1985).

Such above-mentioned interactions were expounded by the XRD technique as well (Fig. 4f). The partial disappearance of the MgSO_4 peaks in 3S-LDO after adsorption in all concentrations (20, 1000, and 2000 mg/L) affirmed that both Mg^{2+} and SO_4^{2-} participated in the MO removal via complexation and EDA interaction, respectively (Rong et al. 2020; Yao et al. 2017). Noticeably, additional peaks at $2\theta=4.54^\circ$, 7.39° , 9.17° , and 61.13° linked to the (003), (006), (009), and (110) planes of LDH were observed at the MO concentration of 2000 mg/L, illustrating that part of MO was adsorbed accompanying with rehydration of LDH via “memory effect” at higher concentration. (Jia and Liu 2019). And the process of inserting into interlayers also caused the change of layer space, resulting in many new peaks appeared at the 2θ values of $15\text{-}30^\circ$ (Yao et al. 2017).

Apart from the EDA interaction, complexation, and “memory effect”, other mechanisms such as van der Waals, hydrogen bonding, and electrostatic forces (Coulomb forces) were generally introduced in MO removal as numerous researches reported (Yao et al. 2017; Zhang et al. 2019b). In this work, the van der Waals interaction was not considered in controlling the MO adsorption because of the chemisorption of 3S-LDO determined by adsorption kinetic (Fig. S4). Likewise, the hydrogen bonding played a negligible role, judging by the unchanged position of O-H peak in 3S-LDO after MO adsorption (FT-IR, Fig. 4a). To investigate the contribution of electrostatic interaction, the zeta potential of 3S-LDO was examined as shown in Fig. S6a. The values of zeta potential nearly maintained zero in the range of 3-11 which indicated the neutral surface charge of 3S-LDO. That is to say, there was no electrostatic interaction between 3S-LDO and MO, in agreement with the results of the pH effect in Fig.

S6b.

Based on the aforementioned analyses, the removal mechanisms of MO on 3S-LDO were comprehensively summarized in Fig. 5. The removal pathway of MO was determined by the initial concentrations. In all concentrations of MO, the removal by 3S-LDO was mainly associated with the sulfate groups (*i.e.*, EDA interaction) and metal complexation, and the EDA interaction was enhanced with the increase of MO concentration. When the concentration increased to 2000 mg/L, the “memory effect” of LDO also played a role in MO removal besides the two interactions discussed above.

Reusability and ionic strength study

The reusability of adsorbent is a critical factor for evaluating the practical applicability in wastewater treatment. In order to test the reusability of 3S-LDO, the consecutive adsorption-regeneration experiments were repeated five times, with the MO concentration of 1000 mg/L. As shown in Fig. 6a, the adsorption capacity of MO still maintained as high as 3100 mg/g after five cycles. The corresponding removal efficiency was ~91%. These results suggested that the prepared 3S-LDO exhibited good stability and reusability for the removal of MO.

In addition, the effect of competitive anions (Cl^- , NO_3^- , and CO_3^{2-}) with different concentrations on the MO (1000 mg/L) adsorption was also investigated to identify the feasibility of 3S-LDO in environmental applications. The results demonstrated that Cl^- and NO_3^- displayed a negligible effect on the MO adsorption ($q_{\text{anion}}/q_0 > 98\%$) in all ion concentrations (Fig. 6b). However, the removal efficiency of MO exhibited a 15% decrease in the presence of CO_3^{2-} (0.02 M) and then kept a stable value at 72% in the concentration range

of 0.04-0.10 M. The decreased removal efficiency was possible because CO_3^{2-} possessed a stronger affinity in solution as compared to other anions, thus competing with MO for adsorption sites (Lei et al. 2017). On the other hand, CO_3^{2-} would combine with metal ions (*i.e.*, Mg^{2+} and Al^{3+}) from LDO to generate insoluble MgCO_3 and Al(OH)_3 , which weakened the surface complexation between the metal ions and MO, thereby leading to a slight decrease in the removal of MO. Notably, the removal capacity of 3S-LDO for MO remained at a high level (≥ 2596 mg/g) when a large number of CO_3^{2-} were present. This result confirmed that the EDA interaction associated with SO_4^{2-} played a vital role in MO removal rather than complexation.

Selective adsorption performance of 3S-LDO

Given that the authentic dye wastewater contains various kinds of dyes, which might compete with target dyes, it is essential to explore the selective adsorption ability of 3S-LDO toward MO in the coexistence with common dyes (Ghaffar et al. 2018). Methylene blue (MB, cationic dye) was selected as competitive dyes because it has different functional groups, surface charges and sizes with MO (Du et al. 2017). As shown in Fig. 7a, the color of the dye mixture solution was dark green after mixing the same volume of MO (100 ppm, the orange vial in Fig. 7a) and MB (50 ppm, the blue vial in Fig. 7a). When 3S-LDO was added to the mixture solution, it clearly can be seen that the color of the mixture solution became blue within 1 h, which was closed to the color of pure MB solution. This phenomenon suggested the high selectivity of 3S-LDO toward MO, which was also confirmed by UV-vis spectra scan (Fig. 7b). After adsorption, the adsorption peak of MO decreased significantly, while that of MB was almost unchanged, verifying the specific adsorption of 3S-LDO for MO.

Adsorption of MO dye in real waters

The MO removal efficiency in three different types of real water samples, including tap water, river water from the Ganjiang River and industrial wastewater from a factory in Jiujiang, Jiangxi province, China, was also explored to further assess the practical application of 3S-LDO. As shown in Fig. 8, the adsorption processes of MO in tap water and river water showed a fair degree of agreement with the adsorption of MO in deionized water. Even in industrial wastewater, the adsorption efficiency of MO could reach up to 73%. In view of these encouraging results, it is reasonable to deduce that the 3S-LDO sample can serve as a promising adsorbent for authentic dyeing effluents.

Conclusion

In summary, a novel three-dimensional sulfate-functionalized MgAl-layered double oxide (3S-LDO) derived from organic layered wastes was synthesized as a superior and recyclable adsorbent for efficient MO removal. Isotherm and kinetic results unveiled the immense MO capacity of 4340.71 mg/g at 298 K with a fast removal rate-limited in 1 hour, which was much higher than the most known adsorbents. The thermodynamic study illustrated the spontaneous and exothermic reaction between MO and the 3S-LDO. Multiple characterizations were synthetically conducted, unveiling that the superior MO removal was associated with sulfate group in 3S-LDO in virtue of the electron-donor-acceptor (EDA) interaction between the S=O (SO_4^{2-}) and N=N (MO). Besides, the “memory effect” and surface complexation of 3S-LDO enhanced the MO adsorption. More importantly, the recycle experiments and coexisting tests highlighted the outstanding reusability as well as explicit selectivity of 3S-LDO. Even in the

authentic water matrices, 3S-LDO exhibited excellent MO removal with a high removal efficiency of 80%. This work is expected to open a new avenue for the reuse/recycling of organic waste to construct functional adsorbent with enormous capacity, excellent reusability, and high selectivity for organic wastewater treatment.

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Author's contribution

Lingjie Zhang: Methodology, Formal analysis, Writing–original draft, Visualization

Siyin Zheng: Validation, Methodology

Peng Li: Reviewing and Editing

Zhongbang Zhu: Validation, Methodology

Youqin Zou: Resources, Methodology

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Project administration, Funding acquisition

Data availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

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Consent to participate Not Applicable.

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Figures

Figure 1

XRD patterns (a) and FT-IR spectra (b) of 3S-LDO and 3D-LDO; The small-angle scattering pattern of 3S-LDO below 5° (a, inset); Survey (c), Mg 1s (d), S 2p (e), and O 1s (f) XPS spectra of 3S-LDO

Figure 2

SEM (a) and Element mapping images (d) of 3S-LDO; TEM (b) and HRTEM images (c) of 3S-LDO

Figure 3

Effect of 3S-LDO dosage on MO adsorption (a); Effect of initial concentration on adsorption of MO by 3S-LDO and 3D-LDO at 25, 35, and 45 °C (b); MO removal efficiency by 3S-LDO (c) and 3D-LDO (d) with increasing initial concentration; Adsorption thermodynamic of MO on 3S-LDO and 3D-LDO (e); Effect of contact time on the MO adsorption by 3S-LDO with different initial concentrations (f) and the inset in the Figure showed the photographs of aqueous solutions of MO before and after adsorption. Above experiments were performed via changing corresponding condition and fixing other conditions. The fixed conditions selected from the following value: dosage of 0.3 g/L, reaction time of 12 h, solution temperature of 25 °C, and MO concentration of 1000 mg/L

Figure 4

FT-IR spectra (a) and the magnified spectra in a wavenumber range of 400–900 cm^{-1} (b) of 3S-LDO before and after MO adsorption with various concentrations; High-resolution Mg 1s and Al 2p XPS spectra (c), S 2p XPS spectra (d), N 1s XPS spectra (e) and XRD patterns (f) of 3S-LDO before and after MO adsorption

Figure 5

The schematic illustration of 3S-LDO adsorption mechanism for MO

Figure 6

The recyclability of the 3S-LDO for the adsorption of MO (a). Effects of ionic strength on MO adsorption by 3S-LDO (b). Experiment conditions: $T=25^\circ\text{C}$, $C_0(\text{MO})=1000\text{ mg/L}$, adsorbent dosage= 0.3 g/L , reaction time= 12 h

Figure 7

The photos of the selective adsorption MO from MO/MB mixture solution (a) and the UV-vis spectra of MO/MB mixture solution before and after adsorption (b) by 3S-LDO. Experiment conditions: $T=25\text{ }^{\circ}\text{C}$, $C_0(\text{MO})=100\text{ mg/L}$, $C_0(\text{MB})=50\text{ mg/L}$, adsorbent dosage= 0.3 g/L , reaction time= 1 h

Figure 8

MO removal efficiency of 3S-LDO in real water samples. Experiment conditions: T=25 °C, C₀(MO)=1000 mg/L, adsorbent dosage=0.3 g/L, reaction time=12 h

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